

2014

CHEMISTRY

(Major)

Paper : 6.1

(Spectroscopy)

Full Marks : 60

Time : 3 hours

*The figures in the margin indicate full marks
for the questions*

1. Answer/Choose the correct answer of the following : 1×7=7
- (a) A molecule undergoes transition from ground state to an excited state. If the **uncertainty in excited state energy level** is 10^{-30} J, calculate the lifetime of the molecule in the excited state.
- (b) What is the lowest vibrational energy in terms of oscillation frequency for a diatomic molecule undergoing simple harmonic motion?
- (c) Show pictorially the symmetric stretching and symmetric bending vibrations of water molecule.

- (d) The term symbol for a particular atomic state is 3S_1 . What are the values of L and J for this state?
- (e) The photoelectron ejected from a diatomic molecule with an energy of radiation 3.4×10^{-18} J has the kinetic energy of 1.0×10^{-8} J. Calculate the ionization energy per mole for this ejection.
- (f) Which of the following statements is true?
- (i) Nuclei with odd mass cannot have half integral spins
 - (ii) Nuclei with both p and n even have non-zero spin
 - (iii) Nuclei with both p and n odd have integral spin
- (g) How many normal modes of vibration does CCl_4 possess?

2. Answer the following briefly : 2×4=8

- (a) Indicate whether C—C stretching vibration in CH_3CCl_3 and symmetric stretching vibration in SO_2 are IR active or not.

- (b) Prove that the mass to charge ratio of an ion in a mass analyzer following a circular path is inversely proportional to the accelerating potential applied.
- (c) How many normal vibration modes are possible for linear ethyne and non-linear benzene molecules?
- (d) Predict the appearance of the high-resolution NMR spectrum of acetaldehyde.

3. Answer any *three* questions of the following :

5×3=15

- (a) What are the factors which determine intensities of spectral lines? Discuss. 5
- (b) Discuss the principle of obtaining Raman spectra of molecules clearly defining Stokes' and anti-Stokes' radiations and Rayleigh scattering. Why are Stokes' lines more intense than anti-Stokes' lines? 4+1=5
- (c) Calculate the moment of inertia of a H₂O molecule around its two-fold axis. The HOH bond angle is 104.5° and the bond length is 95.7 p.m. 5
- (d) Draw the proton NMR spectra of CH₃CH₂Br and CH₃CHBrCH₃. Indicate the approximate chemical shift, fine structure due to spin-spin coupling and the relative intensities of the lines. 5

4. Answer any *three* questions of the following :

10×3=30

(a) (i) Describe how z-components summation method is used to deduce various allowed values of j for ${}^2P_{3/2}$ and ${}^2P_{1/2}$. 3

(ii) Discuss Franck-Condon principle to explain intensities of vibronic transitions due to absorption or emission of a photon of appropriate energy. 5

(iii) How does isotopic effect change the position of microwave band? 2

(b) (i) Write the difference between fluorescence and phosphorescence. 5

(ii) Which of the following systems will show ESR spectrum? Give reasons : 5

H, Na^+ , ${}^\bullet\text{CH}_3$, NO_2 , H_2

(c) (i) Discuss the vibration-rotation spectrum of CO. 5

(ii) Describe what is chemical shift taking the example of an alkane. 5

- (d) (i) Give a highly schematic diagram of a mass spectrometer. 3
- (ii) Mention four methods of ionizing sample molecules entering the ion source unit in a mass spectrometer. Discuss one method in detail. 5
- (iii) Explain, with two examples, what is nitrogen rule in mass spectrometry. 2
- (e) (i) Explain the fine structure of electronic spectrum of atomic hydrogen. 5
- (ii) The wavelength of a radiation absorbed is found to be 500 nm. Express this in terms of wave number, frequency and energy. 3
- (iii) A compound with molecular formula C_7H_5N shows the following prominent IR bands :
3050, 2240, 1600, 1500, 750, 700
(all in cm^{-1})
Predict the structure of the molecule. 2
- (f) (i) What are spherical and symmetric rotors? 5

- (ii) The ratio of I_0/I is 1.98 for the absorption by a compound at a specific wavelength. If the concentration of the sample is 0.9 M and path length is 0.01 m, find the molar extinction coefficient. 2
- (iii) Using IR spectra, how will you distinguish between ethanol and ethanal? 3

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